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(54) PROCESS FOR THE HYDRATION OF OLEFINS TO PRODUCE ALCOHOLS AND ETHERS

(71) We, RHEINPREUSSEN AKTIENGESELLSCHAFT FÜR BERGBAU UND CHEMIE, a German Company, of Homberg/Niederrhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the production of alcohols and ethers by the direct addition of water to lower olefins.

The carrying out of such process in the presence of a solid acidic catalyst is well known from the patent literature.

Inorganic catalysts, such as sulphuric acid or phosphoric acid on silica, alumina, bentonite or tungsten oxide have been proposed for use in such reaction. However, these catalysts only give satisfactory space-time yields at temperatures above 260°C. As a result of the disadvantageous equilibrium position at such temperatures, only a small amount of the olefin feed is converted, so that recycle or more than one pass is necessary. The life of these catalysts with respect to water in the liquid phase is very poor and wholly unsatisfactory (see Brennstoff-Chemie, Vol. 34, page 330, Year 1953).

It is also known to use organic catalysts which contain strongly acidic groups (German Patent Specification No. 866,191, United States Patent Specification No. 2,477,380, German Auslegeschriften Nos. 1,105,403, 1,210,768 and 1,168,909; Industrial & Engineering Chemistry, Product Research and Development, Vol. 1, No. 4, December 1962, pages 296 and following.) These catalysts are strongly acidic ion exchangers, in which the sulphonic acid groups are, without exception, linked to aromatic carbon atoms.

These ion exchange resins have a much higher resistance to water in the liquid phase than have the aforementioned inorganic catalysts; however, as is evident from Runs A and B which are hereinafter given, they loose by hydrolysis a considerable proportion of their sulphonic acid groups within relatively short periods of from 600 to 1000 hours at the temperatures of 120°—150°C required for the direct hydration.

Catalysts which are so inadequate are unsuitable for the synthesis of products on a large industrial scale, such as isopropanol, sec. butanol, diisopropyl ether and di-sec-butyl ether. It is also desirable to find catalysts which can be operated at higher temperature.

It is also known from the literature that aliphatic sulphonic acids have considerable resistance to hydrolysis, whereas aromatic sulphonic acids hydrolyse almost quantitatively at a temperature of about 170°C (see Klages Lehrbuch der Org. Chemie, Vol. I, page 726 (1959)).

Surprisingly, it has been found that polymers or resins containing sulphonic acid groups linked or bound to non-aromatic carbon atoms are very suitable for use as catalysts in the direct hydration of straight-chain olefins, particularly olefins containing not more than 12 carbon atoms in the molecule.

According to the invention therefore, there is provided in a process for the direct hydration of the double bond of an olefin at elevated temperature and elevated pressure, the improvement which comprises carrying out the hydration in the presence, as catalyst, of a sulphonic acid cation exchange resin in which

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the sulphonic acid groups are bound to non-aromatic carbon atoms.

According to the invention furthermore, there is provided a process for the production of an alcohol, which comprises subjecting an olefin to direct hydration at a temperature in the range 110—170°C and at a pressure in the range 40—160 atmospheres gauge in the presence, as catalyst, of a sulphonic acid cation exchange resin in which the sulphonic acid groups are bound to non-aromatic carbon atoms.

The non-aromatic carbon atoms to which the sulphonic acid groups are bound in the cation exchange resins are preferably aliphatic carbon atoms.

The cation exchange resin used in the process according to the invention affords the following advantages:—

1. It is substantially resistant to hydrolysis at temperatures of from 150° to 160°C.

2. No or substantially no polymeric hydrocarbons are produced when it is used as catalysts in the direct hydration process.

3. It operates with remarkable selectivity according to the water-to-olefin molar ratio, the cross-sectional load and the reaction temperature employed. The ether constituent of converted olefins may amount to from 2—25% according to the reaction conditions.

4. Recycling of the unconverted olefin is unnecessary, since 70% or more of the olefin feed can be converted in a single pass.

The catalyst may have a resin matrix which is essentially that of, or is derived from, a styrene-divinylbenzene copolymer or a polymer or copolymer of an unsaturated aldehyde or unsaturated ketone, for example, polyacrolein, acrolein-divinylbenzene copolymer or methyl isopropenyl ketone-divinylbenzene copolymer. Thus, for example, the catalyst may be produced by polymerisation of acrolein or copolymerisation of acrolein with divinylbenzene, addition of H_2S to the polymer, and oxidation with H_2O_2 to the sulphonic acid (German Auslegeschrift No. 1,237,322).

Starting from a styrene-divinylbenzene copolymer, a suitable cation exchange resin in which the sulphonic acid groups are aliphatically bound was produced as follows:—

100 grams of a styrene-divinylbenzene copolymer in pearl form comprising 97% by weight of styrene units and 3% by weight of divinylbenzene units were pre-swollen with 600 ml. monochlorodimethyl ether for thirty minutes and then heated for two hours under reflux while adding 50 grams of anhydrous zinc chloride. The polymer was then drawn off by suction, taken up in or transferred to water and washed with water until the wash water was neutral. After drying, 138 grams of a dark resin containing 22% by weight of chlorine was obtained.

This resin together with 140 ml. dimethyl sulphide and a sufficient amount of ethanol was heated to reflux temperature with stirring, so that a temperature of 57—58°C was produced in the reaction vessel. The mixture was cooled after six hours and washed first with alcohol and then with water. The resin swelled in water, and it was heated with 140 grams of sodium sulphite and 420 ml. of water for 48 hours at 100°C. The sulphite was then removed from the reaction product by washing with water, followed by activation with dilute hydrochloric acid and washing with water until the product was substantially free from chlorine, after which the resin was dried. 160 grams of a sulphonic acid cation exchange resin containing only traces of chlorine and having an acid number of 180 mg.KOH/g. were obtained.

A suitable catalyst may also be prepared by copolymerising vinyl sulphonic acid and divinylbenzene.

The production of alcohols and ethers by the direct addition of water to olefins in accordance with the invention is preferably carried out at a temperature in the range 125°—150°C, and at a pressure in the range 60—120 atmospheres gauge. The catalyst is suitably used in the form of a stationary or fixed bed and the reactants may be passed in concurrent or countercurrent flow relation over it. The water to olefin molar ratio is advantageously from 1:1 to 50:1, preferably from 5:1 to 30:1, and the cross-sectional catalyst load is advantageously from 1 to 40 mols H_2O/sq. cm., preferably from 5 to 25 mols H_2O/sq. cm.

The olefin suitably contains not more than 12 carbon atoms in the molecule. Thus the olefin may suitably be an isoolefin containing 4 to 12 carbon atoms in the molecule. Preferably, the olefin contains not more than 6 carbon atoms in the molecule and particularly suitable olefins include propylene and butylenes, especially isobutylene.

The invention is illustrated in the following Examples 1 to 5. Runs A and B are given by way of comparison, and in Runs A and B the hydration is effected in the presence of a cation-exchange resin, in which the sulphonic acid groups are bound to a carbon atom of an aromatic ring. It will be clearly seen from the results obtained in the two Runs that the olefin conversion drops substantially and that the resistance of the catalyst to hydrolysis is also substantially lower than that of the catalyst used in the process according to the invention, particularly when the reaction temperature is increased from 135°C to 150°C. The elimination of sulphonic acid groups by hydrolysis is perceptible from the reduced sulphur content of the catalyst.

These disadvantages associated with Runs A and B are mitigated by using, as catalyst, a cation exchanger in which the sulphonic acid groups are bound to a carbon atom of an aliphatic carbon chain.

RUN A

For the synthesis, 100 mols (1800 grams) of H_2O and 5.6 moles (225 grams) of propylene per hour were fed by means of a double-piston metering pump to a V4A trickling reactor having a length of 3000 mm. and an internal width of 26 mm., which was heated by a steam jacket and provided with a preheating vessel for vapourising the liquid propylene feed, and also a heatable settling tank for separate withdrawal of the liquid phase and of unconverted residual gas. A reaction temperature of 135°C was employed. The catalyst was a sulphonated styrene polymer cross-linked with 8% divinylbenzene. A pressure of 95 atmospheres gauge was employed. The space-time yield was determined over successive intervals during the test. The sulphur content of the catalyst was determined at the given time intervals by withdrawal of small samples. The results are shown in Table A.

TABLE A

Hours of Operation	Mols of olefin converted per litre of catalyst per hour	sulphur content of the catalyst %
0	2.60	16.5
35	2.52	15.9
55	2.46	15.5
90	2.40	15.1
150	2.30	14.7
240	2.21	14.2
320	2.15	14.0
400	2.08	13.8
500	2.00	13.6
600	1.93	13.4
700	1.87	13.4
800	1.82	13.0
900	1.76	12.8
1000	1.70	12.6

RUN B

Run A was repeated but with the modification that the reaction temperature was 150°C. The results are shown in Table B.

TABLE B

Hours of Operation	Mols of olefin converted per litre of catalyst per hour	Sulphur Content of the catalyst %
0	4.0	16.5
50	3.8	15.3
100	3.1	14.5
200	2.7	13.1
300	2.3	12.4
400	1.9	11.8
500	1.7	11.4
600	1.5	10.6

EXAMPLE 1

A cation exchange resin produced by the copolymerisation of methyl isopropenyl ketone with 8% by weight of divinylbenzene, addition of H_2S and oxidation with hydrogen peroxide to produce sulphonic acid, served as catalyst. The hydration of propylene was carried out in the manner described in Run A except that a reaction temperature of 140°C was employed. The results are shown in Table 1.

TABLE 1

Hours of operation	Mols of olefin converted per litre of catalyst per hr.	Sulphur content of the catalyst %
0	2.25	14.7
250	2.23	14.5
500	2.20	14.3
750	2.15	14.2
1000	2.10	14.0

Table 1 shows the substantial constancy of olefin conversion and the considerably increased stability of the catalyst, in the process according to the invention.

EXAMPLE 2

Example 1 was repeated but with the modification that the reaction temperature used was 150°C. The results are shown in Table 2.

TABLE 2

Hours of operation	Mols of olefin converted per litre of catalyst per hour	Sulphur content of the catalyst %
0	3.7	15.2
500	3.5	14.6
750	3.4	14.4
1000	3.3	14.2

EXAMPLE 3

The cation exchange resin used in this Example was produced by the copolymerisation of 4 mols of vinyl sulphonic acid and 1 mol of divinylbenzene. The apparatus described in Run A was used for the hydration of propylene. The reaction temperature was 140°C and a pressure of 95 atmospheres gauge was employed as in Runs A and B and Examples 1 and 2. The results obtained are shown in Table 3.

TABLE 3

Hours of operation	Mols of olefin converted per litre of catalyst per hour	Sulphur content of the catalyst %
0	2.30	15.3
800	2.18	14.8

EXAMPLE 4

The hydration of propylene was carried out as in Example 3 except that a pressure of 60 atmospheres gauge and a reaction temperature of 135°C were employed. The results are shown in Table 4.

TABLE 4

H_2O through-put mol/litre of catalyst/hr.	Propene through-put, mol/litre of catalyst/hr.	Propene converted mol/litre catalyst per hr.	Analysis	
			IPA* %	C_3-ether %
47	4.3	2.0	97.0	3.0
36	4.3	1.9	96.3	3.7
25	4.3	1.75	95.0	5.0
11	4.3	1.65	93.0	7.0
5	4.3	1.60	90.0	10.0

*IPA = isopropyl alcohol.

EXAMPLE 5

The process was carried out as described in Example 4 except that a pressure of 100 atmospheres gauge was used under varying loads. The results are shown in Table 5.

TABLE 5

H_2O supplied, mols per hour	Propene supplied, mols per hour	Propene converted %	Propene converted, mols/litre catalyst per hour	Analysis	
				IPA %	Ether %
66.7	7.34	47	2.30	96.60	3.40
66.7	6.18	56	2.31	96.59	3.41
66.7	5.67	61.5	2.33	96.59	3.41
66.7	5.01	70.0	2.34	96.59	3.41
66.7	4.53	75.0	2.27	96.75	3.25
66.7	3.86	82.5	2.13	97.00	3.00
66.7	3.15	86.5	1.82	97.30	2.70
66.7	1.75	92.5	1.08	97.67	2.33

WHAT WE CLAIM IS:—

1. In a process for the direct hydration of the double bond of an olefin at elevated temperature and elevated pressure, the improvement which comprises carrying out the hydration in the presence, as catalyst, of a sulphonic acid cation exchange resin in which the sulphonic acid groups are bound to a non-aromatic carbon atom.

2. A process for the production of an alcohol, which comprises subjecting an olefin to direct hydration at a temperature in the range 110—170°C and at a pressure in the range 40—160 atmospheres gauge in the presence, as catalyst, of a sulphonic acid cation exchange resin in which the sulphonic acid groups are bound to a non-aromatic carbon atom.

3. A process according to claim 1 or claim 2, in which the sulphonic acid groups are bound to aliphatic carbon atoms.

4. A process according to any one of the preceding claims, in which the direct hydration is carried out at a temperature in the range 125—150°C and at a pressure in the range 60—120 atmospheres gauge.

5. A process according to any one of the preceding claims, in which the olefin contains not more than 12 carbon atoms in the molecule.

6. A process according to any one of the preceding claims, in which the olefin contains not more than 6 carbon atoms in the molecule.

7. A process according to any one of the preceding claims, in which the olefin is a butylene.

8. A process according to any one of claims 1 to 6, in which the olefin is propylene.

9. A process according to any one of the preceding claims, in which the catalyst is present as a fixed or stationary bed.

10. A process according to claim 8, in which the reactants are passed concurrently over the catalyst.

11. A process according to any one of the preceding claims, in which the molar ratio of water to olefin is from 1:1 to 50:1.

12. A process according to any one of the preceding claims, in which the molar ratio of water to olefin is from 5:1 to 30:1.

13. A process according to any one of the preceding claims, in which the cross-sectional catalyst load is from 1 to 40 gram-mols of water per square centimetre.

14. A process according to claim 13, in which the cross-sectional catalyst load is from 5 to 25 gram-mols of water per square centimetre.

15. A process according to any one of the preceding claims, in which the resin matrix is essentially that of, or is derived from, a styrene-divinylbenzene copolymer.

16. A process according to any of claims 1 to 14, in which the resin matrix is essentially that of, or is derived from, a polymer or copolymer of an unsaturated aldehyde or unsaturated ketone.

17. A process according to claim 16, in which the resin matrix is essentially that of, or is derived from, polyacrolein or an acrolein-divinylbenzene copolymer.

18. A process according to claim 16, in which the resin matrix is essentially that of, or is derived from, a copolymer of methyl isopropenyl ketone and divinyl benzene.

19. A process according to any one of claims 1 to 14, in which the catalyst is a copolymer of vinyl sulphonic acid and divinylbenzene.

20. A process for the production of an alcohol by the direct hydration of an olefin, substantially as hereinbefore described in any one of Examples 1 to 5.

21. An alcohol whenever obtained by the process claimed in any one of the preceding claims.

22. An ether whenever obtained by the process claimed in any one of claims 1 to 20.

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